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THE STORABILITY AND THERMAL STABILITY
OF SOLUTIONS OF 10 TO 30% AMMONIUM PERCHLORATE
IN HYDRAZINE

By

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ABSTRACT

The storability of solutions of 10 to 30% (W/W) of ammonium perchlorate in hydrazine was established by determining that their ullage pressures at temperatures from 50° to 75°C (122° to 167°F) remained constant for over 7 months; the freezing points of these solutions ranged from about -5° to -25°C (23° to -13°F). The thermal stability at higher temperatures was determined by JANAF Method No. 6; with this equipment, it was possible to determine that solutions of 10 to 30% ammonium perchlorate may be stored at temperatures in the vicinity of 80°C (176°F) for as long as 18 hours without rupture of 1800-psig diaphragms, but detonation occurred within one hour at about 100°C. The solutions detonated at about 160°C (320°F) when heated at rates in excess of 10°C per minute; at similar heating rates, hydrazine did not detonate, but it rapidly generated pressure at 220°C (428°F) and ruptured 1800-psig burst-diaphragms in the JANAF apparatus.

INTRODUCTION

The observation that solutions of ammonium perchlorate in hydrazine appear to have low freezing points prompted interest that such mixtures might have applications as monopropellants in systems where a much lower freezing point than hydrazine is required.

Solutions of ammonium perchlorate in hydrazine are equilibrium mixtures containing hydrazine perchlorate and dissolved ammonia:

$$N_2H_4 + NH_4ClO_4 \rightleftharpoons N_2H_5ClO_4 + NH_3$$
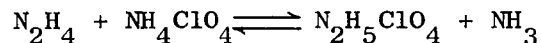
Accordingly, when these solutions are frozen, they exhibit the impact sensitivity of solid hydrazine perchlorate and some experiments at JPL showed that the frozen mixtures are indeed shock sensitive. Additionally,

1

it was anticipated that the thermal stability of the solutions would be considerably lower than hydrazine alone because of the presence of perchlorate. In fact, before the mixtures of ammonium perchlorate and hydrazine could be given further consideration as monopropellants, it was necessary to determine whether they could be stored without slow generation of gaseous pressure at the temperature indigenous to rocketry (-60°C to +60°C), and whether they would show tendencies to detonate or decompose violently at temperatures expected to be encountered in the coolant passages or in the injectors of rockets or gas generators.

Reagents

The hydrazine used in the determinations (Matheson, Coleman, and Bell) assayed as follows:

|	
H_2O	1.91%
NH_3	0.06%
$C_6H_5NH_2$	0.16%

The ammonium perchlorate (Fisher Scientific, analytical-reagent grade) was used as received; its assay is known to be in excess of 99.5% (from prior work at JPL) and its water content seldom exceeds 0.1%.

VAPOR PRESSURE AND STORABILITY

The initial work on solutions of ammonium perchlorate in hydrazine involved fabrication of an apparatus which would permit measuring vapor pressures at temperatures up to 60°C and determining whether decomposition occurred slowly. The results from this work would determine not only whether the solutions were storable, but also whether it would be advisable to invest funds to determine thermal stability at elevated temperature; clearly, if a candidate monopropellant can not be prepared and stored, there is little reason to continue its investigation. It was recognized that the solutions would have equilibrium vapor compositions consisting of ammonia and hydrazine and that the vapor pressures

developed would be, in the main, due to ammonia, and that all solutions would have to be prepared and treated so as to prevent loss of ammonia at any time during the anticipated long storage terms.

If decomposition of hydrazine were to be catalyzed by the presence of perchlorate, then the apparent vapor pressure would increase with time, slowly if the decomposition were to generate a preponderance of ammonia (which is quite soluble in hydrazine), and rapidly if nitrogen or hydrogen were evolved:

$$(3 + x)N_2H_4 \longrightarrow 4NH_3 + (1 + x)N_2 + 2xH_2$$

$$N_2H_4 \longrightarrow N_2 + 2H_2$$
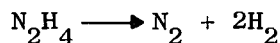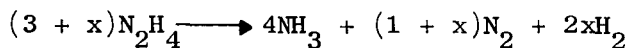
Oxidative reactions of hydrazine and ammonium perchlorate would be detected by an increase in pressure from liberated nitrogen, but it would not be possible to determine from the pressure increment whether oxidation or catalysis is responsible:

$$4NH_4ClO_4 + 5N_2H_4 \longrightarrow 7N_2 + 16H_2O + 4HCl$$
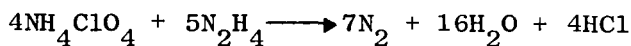
On the other hand, if the oxidative reaction were to result in a tetrazane, e.g.,

$$8N_2H_4 + NH_4ClO_4 \longrightarrow 4NH_2NHNHNH_2 + 4H_2O + NH_4Cl$$
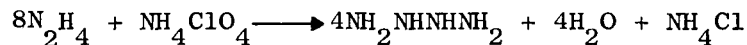
the formation of water would scarcely be detectable except that there might be a drop in apparent vapor pressure due to the enhanced solubility of ammonia in water. If the tetrazane formation were to occur with concomitant formation of nitrogen,

$$10N_2H_4 + 2NH_4ClO_4 \longrightarrow N_2 + 2HCl + 8H_2O + 5NH_2NHNHNH_2 \quad ,$$
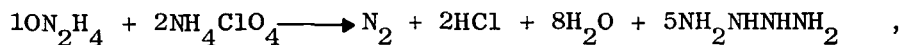
the decrease in pressure due to the increased solubility of ammonia in the generated water might offset the increase in pressure due to niteogen, and the oxidation would remain essentially undetected. Of course, the detection of a substantial increase in water content in the mixtures

3

would be ample evidence that oxidation reactions took place, but the water analysis would have to wait until the end of a prolonged storage period.

Many types of equipment were considered before the apparatus indicated in Figure 1 was selected. Chief among the considerations was the use of nonmetal systems to avoid the possibility of catalytic decomposition of hydrazine and thus lead to an erroneous indication of the instability of the monopropellant system; prior work at JPL had indicated that hydrazine and ammonium perchlorate were by themselves stable in glass systems containing mercury. The apparatus was limited to essentially one atmosphere of pressure because of the mercurial barometer leg (Figure 1), but this was not considered a deterrent since available data indicated that the partial pressure of hydrazine and the partial pressure of ammonia dissolved in hydrazine would barely total 760 mm at temperatures of interest for long-term storage.

The apparatus designed to observe vapor pressure and storability of these solutions is shown in Figure 1. The apparatus consisted of a sample chamber that was connected to a 80-cm side arm. The entire unit was housed in a large-diameter glass heater designed to maintain the sample chamber and the resulting mercury column at a uniform temperature by a winding of resistance wire. The temperature of the system could be varied from room temperature to about $100^{\circ}C$ by controlling energy input with a variable autotransformer.

Three long-term storage samples were prepared with concentrations of ten, twenty, and thirty per cent (W/W) ammonium perchlorate in hydrazine. Each sample solution was placed in the sample chamber (Figure 1) via a short open neck at the top of the chamber. The solution was frozen by liquid nitrogen while the side arm was immersed in mercury, and the system was evacuated through the sample entry port. After the system was evacuated entirely, the entry port was sealed-off with a hand torch. Each storage unit was placed within its glass heater unit and the temperature was adjusted by means of a variable autotransformer. As the temperature increased, the vapor pressure of hydrazine and the pressure of the ammonia produced by reaction of N_2H_4

4

METER
STICK

SAMPLE
CHAMBER

THERMOMETER

MERCURY
COLUMN

HEATER
COILS

POWER
REGULATOR
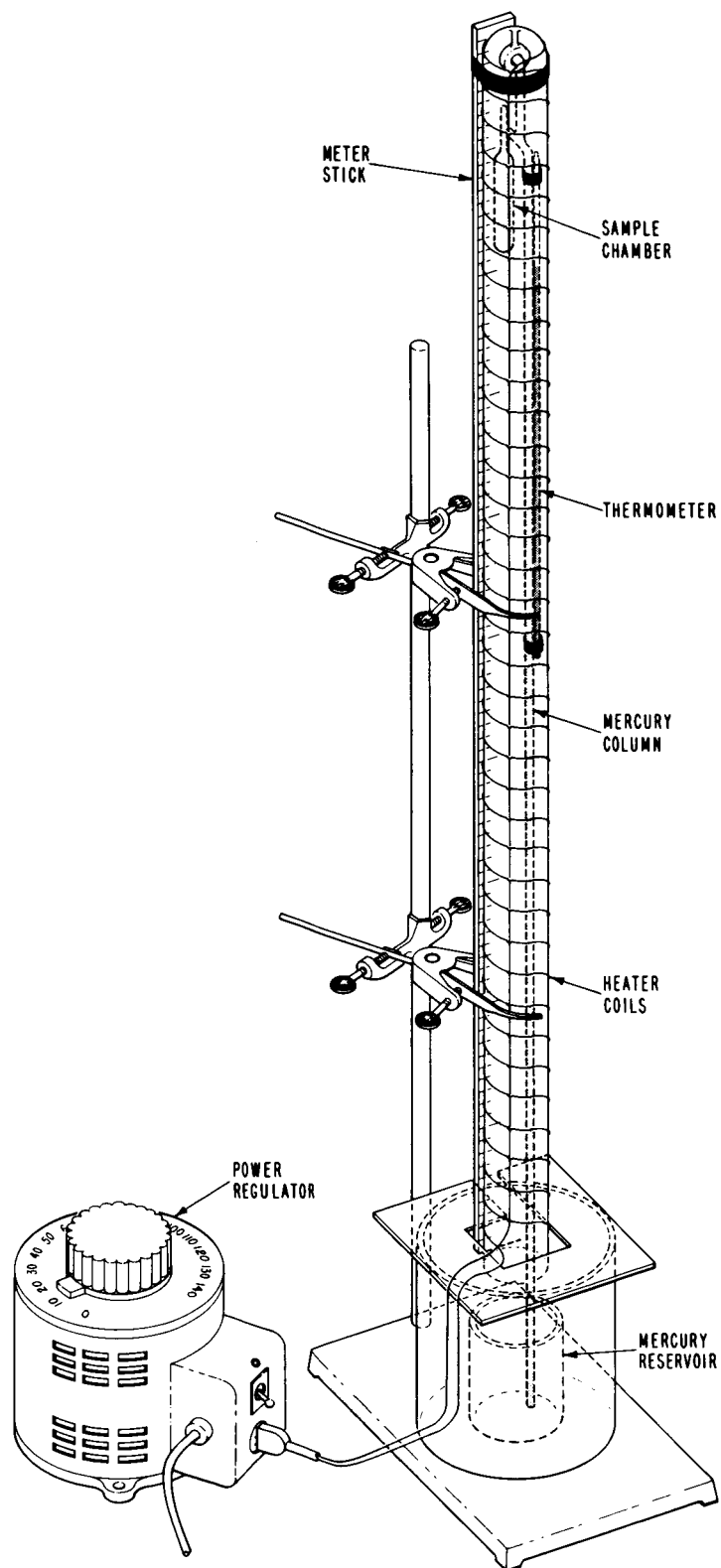
MERCURY
RESERVOIR

TC—106591—18

FIG. 1 APPARATUS FOR OBSERVING THE VAPOR
PRESSURE AND STORABILITY OF $NH_4ClO_4 - N_2H_4$
MIXTURES

5

with NH_4ClO_4 depressed the mercury column. The temperature of each unit was gradually increased over a period of several days in small increments in order to observe the stability of the N_2H_4-NH_4ClO_4 mixture with increasing temperature. Any rapid depression of the mercury column would have indicated decomposition of the sample. The pressures within the columns at each temperature were noted and plotted. Final storage temperatures (selected to give about one atmosphere of pressure) were as follows:

Wt-% NH_4ClO_4 in N_2H_4	Temperature, ^oC
10	75
20	60
30	52

The curves shown in Figure 2 represent the combined vapor pressures of hydrazine and ammonia over the 10, 20, and 30% solutions with increasing temperature. It can be seen that the effect of a greater concentration of ammonium perchlorate and hydrazine is to increase the vapor pressure, presumably due to a higher concentration of ammonia formed by the equilibrium reaction:

$$N_2H_4 + NH_4ClO_4 \rightleftharpoons N_2H_5ClO_4 + NH_3$$
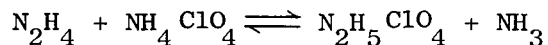
After the final adjustments in storage temperatures were made, the mercury column height and sample temperature for each test were examined periodically over a seven-month period.

No evidence of decomposition was observed for any of the mixtures at their storage temperatures during the seven-month period; the mercury columns remained at essentially constant levels throughout the storage term. At the end of the storage term, the solutions remaining in the sample bulb were analyzed for their water content in order to detect if nonpressure-developing oxidative reactions had occurred. No significant increase in water content was detected.
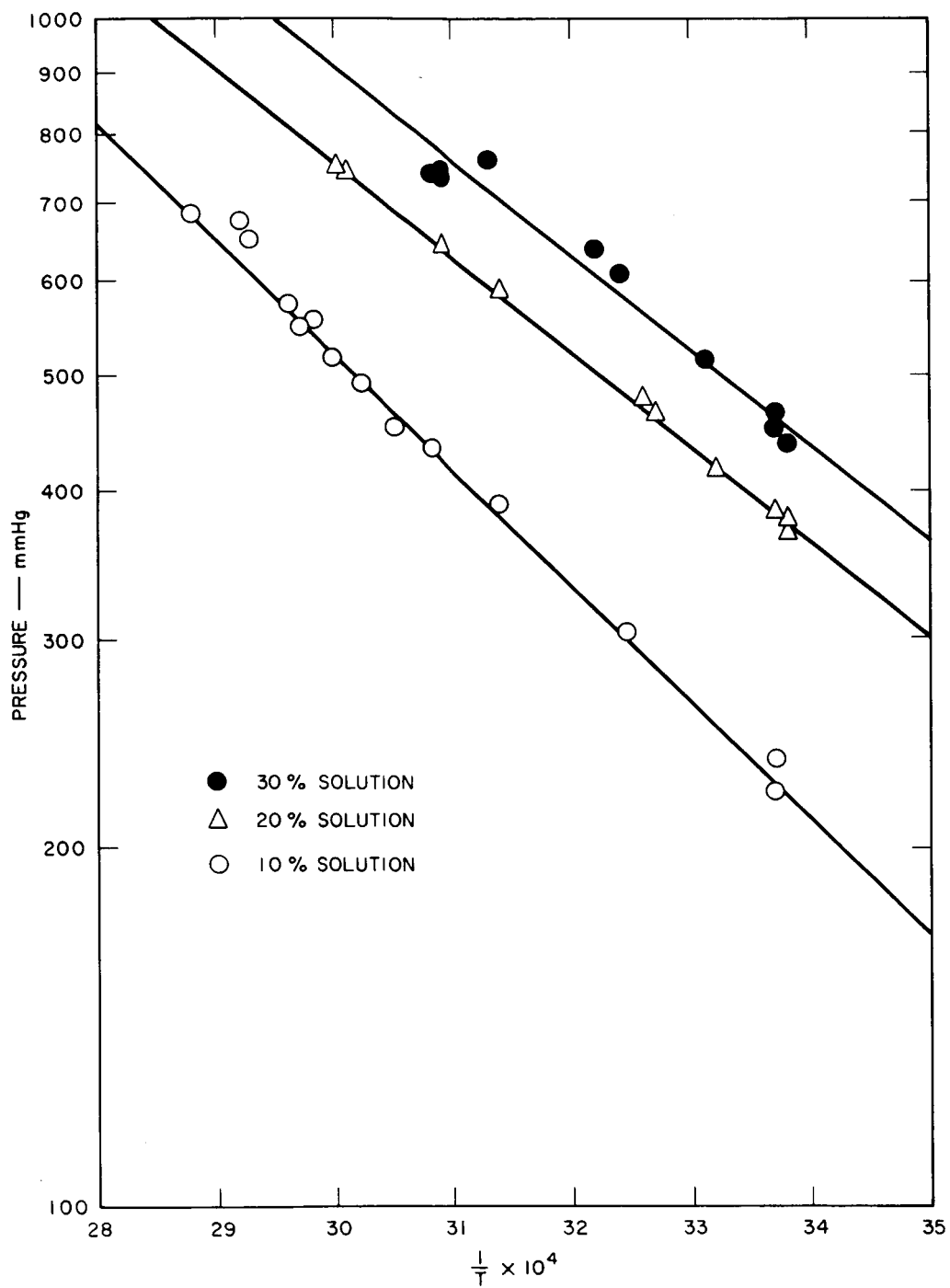
FIG. 2 VAPOR PRESSURE CURVES OF SOLUTIONS OF NH_4ClO_4 IN N_2H_4
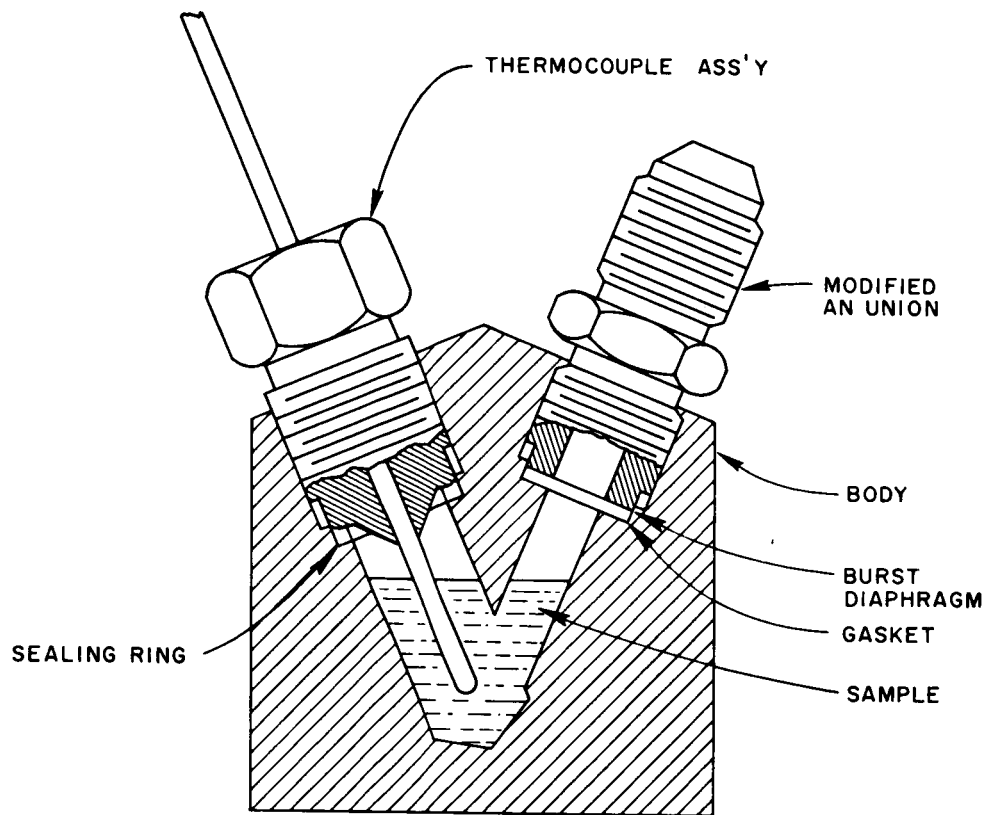
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THERMAL STABILITY DETERMINATIONS

The apparatus and procedure used for the determination of the thermal stability of ammonium perchlorate-hydrazine mixtures is essentially that described in JANAF Method No. 6 for testing the stability of monopropellants, and consisted of a heating bath and a small stainless steel bomb that was fitted with a thermocouple well and a replaceable burst-diaphragm. A schematic diagram of the bomb is shown in Figure 3. The internal volume of the bomb, with fittings in place, was about 1.3 cc. The burst-diaphragms were made of aluminum and designed to fail at 1800 ± 100 psi at room temperature, as determined by hydrostatic testing.

The bath for heating the loaded bomb was a hexagonal aluminum block, about 4.5 inches across, bored out to contain the bomb, and heated by six 250-watt strip-heaters. Three of these were maintained at a constant level of heat input by a variable transformer; the other three were controlled by a temperature regulator.

For safety, the entire operation was conducted outdoors and within a heavy plywood shelter; the operator and controls were about 50 feet away. The bomb was mounted on a steel shaft which could be raised and lowered remotely by a bead-chain and pulley arrangement. A vibrator was attached to the shaft to agitate the bath and the sample. Figure 4 shows a general layout of the apparatus.

Two recorders were connected to measure temperature differences between the sample within the bomb and the bath. Since the recorders were of the null-balance type and of inherently high resistance, there were no problems with parasitic currents or shunting effects between the two thermocouples. The recorder which was used for sample temperature measurements had a chart speed of about 1 cm/min and the chart was graduated from 0 to 10 mv for an iron-constantan thermocuple, which corresponds to a temperature range of $0^{\circ}C$ to about $200^{\circ}C$. A 10-mv bucking voltage was included in the circuit so that it could be switched on to extend the recorder range an additional 10 mv. The differential temperature recorder was the same as the sample temperature recorder but it

THERMOCOUPLE ASS'Y

MODIFIED
AN UNION

BODY

BURST
DIAPHRAGM

GASKET

SAMPLE

SEALING RING

SCALE: ABOUT TWICE ACTUAL SIZE

TA-6063-33

FIG. 3   THERMAL STABILITY BOMB SCHEMATIC DIAGRAM

THERMO-
COUPLE

BOMB

SAMPLE
TEMPERATURE
RECORDER

DIFFERENTIAL
TEMPERATURE
RECORDER

HEATING
BATH

BATH
TEMPERATURE
CONTROLLER
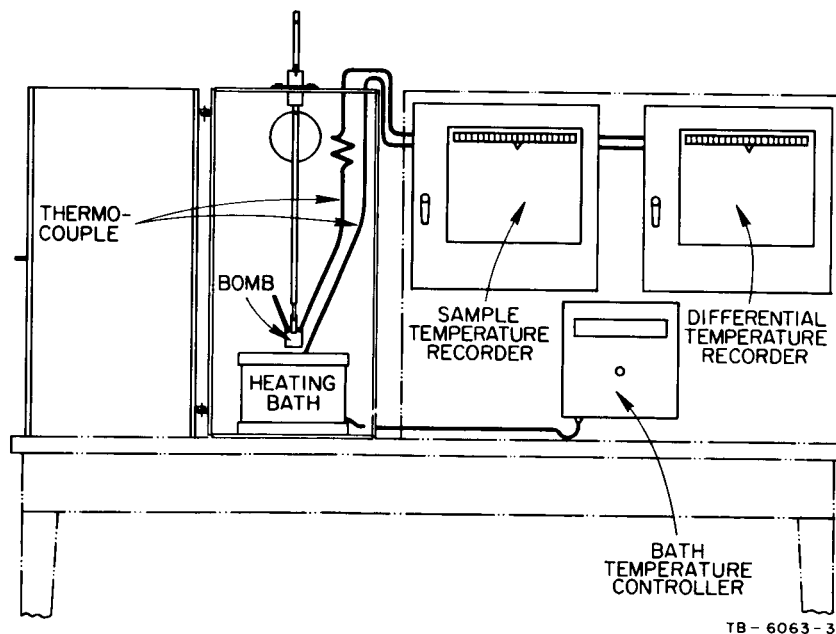
TB-6063-34

FIG. 4   THERMAL STABILITY TEST EQUIPMENT ASSEMBLY

was not connected to a bucking voltage source because the recorder was only to indicate the difference in temperature between the bath and the sample, and this value rarely exceeded 3 mv.

The sample thermocouple was made of 30-gage iron and constantan wire protected by a 1/16-inch o.d. stainless steel sheath, welded at the tip. The junction was electrically insulated from the sheath to avoid a short circuit path through the sheath, bomb, and the bath to the other thermocouple. The bath and reference thermocouples were of 16-gage iron and constantan wire and were also electrically-insulated to avoid short-circuits. The thermocouples and the entire differential system were appropriately calibrated.

The stainless steel bomb shown in Figure 3 was loaded with a freshly-prepared ammonium perchlorate-hydrazine solution; then the sample thermo-couple and the burst diaphragm were screwed into place and the bomb was fastened to the lowering shaft just above the heating bath. A sample volume of about 0.5 ml, leaving an ullage of about 0.8 ml, was used for these determinations. (Computations showed that the detonation of 1 ml of nitroglycerine in the bomb was within the safety regulations and bulwarks set up for this program of work.) It was considered desirable to minimize the sample volume; samples smaller than 0.5 ml, however, were not used because the solutions could not make contact with the thermocouple. Before the bomb was lowered into the heating bath, the bath was heated from 20° to 30°C above the sample temperature so that when the bomb was lowered into the bath, the sample temperature would increase monotonically during the test.

Initial bath temperatures and heating rates were such that the total time for a test was between 6 and 12 minutes. This duration was chosen, somewhat arbitrarily, so that tests were long enough for steady-state heating conditions to become established (i.e., constant temperature difference between bath and sample), but short enough to avoid sub-stantial degradation of the sample before the temperature range was reached in which rapid reaction took place. To determine the maximum temperature attainable before degradation and detonation occurred, the

bomb was lowered into the bath before heat was applied and the bath and sample were heated together in a stepwise fashion, holding the sample at each increment for a prolonged interval (about 30 minutes). The vibrator was in operation throughout the tests since it was desirable to increase heat transfer rates between the bath and sample and to minimize temperature gradient in the sample.

After several attempts to determine the approximate maximum temperature at which mixtures of hydrazine and ammonium perchlorate were stable, it became evident that two distinctly different types of burst-diaphragm failures were being encountered. The first type occurred when the testing period spanned less than 15 minutes and the sample temperature was increased monotonically up to its detonation point. The second type occurred when attempts were made to find the maximum temperature that could be maintained without causing a burst-diaphragm failure. Here, the testing periods spanned intervals of greater than 15 minutes, and the temperature was increased slowly in a stepwise fashion and held for a long interval of time at each step.

The first type of burst-diaphragm failure clearly is a result of a detonation, for the burst-diaphragm was punched out cleanly. In most cases, a loud report could be heard easily in the control room 50 feet from the remotely-controlled apparatus. The bomb was always dry and free of residue after the detonations which resulted from rates of heating greater than $10^{o}C/min$; in these instances the detonation temperature was in the vicinity of $160^{o}C$. When the rate of heating was decreased to less than $10^{o}C/min$ but greater than $5^{o}C/min$, the detonations occurred at about $170^{o}C$. As previously mentioned, the duration of these tests was less than 15 minutes and the length of time the samples were maintained above $100^{o}C$ was less than 10 minutes.

The second type of burst-diaphragm failure occurred at much lower temperatures (in the vicinity of $100^{o}C$) when a sample was maintained for prolonged periods of from 10 minutes to 1-1/2 hours at constant temperature. Here, the burst diaphragm failure presumably was due to pressure increases from catalytic or partial oxidative decomposition of

hydrazine accelerated by the presence of the perchlorate. Although the burst-diaphragms were punched out cleanly as if by detonation, the loud reports clearly associated with detonations as noted above were seldom heard and there was, in all these cases, a residue of hydrazine perchlorate, ammonium perchlorate, ammonium chloride, or a complex mixture of these compounds. The residue was ignitable.

In an attempt to determine whether the stainless steel bomb material itself or traces of chloride residues were catalyzing the decomposition of the hydrazine, pure hydrazine was heated in the bomb; it was presumed that the rate of decomposition was much slower because when the diaphragms failed they were convex and the ruptures were thin hair-line cracks, not cleanly-punched holes. Further, the pure hydrazine samples could be heated to about 220°C before the burst diaphragms failed. Hence, it was concluded that the perchlorate and not the stainless steel was causing the decomposition of hydrazine. The stainless steel in the bomb was passivated by treatment with nitric acid in an attempt to determine whether catalysis was occurring at sites activated by chloride ion from previous runs, but no difference in results was observed.

The results of the detonation determinations are summarized in Tables I and II. The stability at about 100°C for mixtures containing about 20% ammonium perchlorate is indicated in Table III.

Table I

DETONATION TEMPERATURES OF N_2H_4-NH_4ClO_4 MIXTURES
(Rate of heating less than 10°C/min
but greater than 5°C/min)

% NH_4ClO_4	Detonation Temperature, °C
8.8	178
10.5	171
22.1	172
29.2	166
32.3	168

Table II

DETONATION TEMPERATURES OF N_2H_4-NH_4ClO MIXTURES
(Rate of heating greater than 10°C/min)

% NH_4ClO_4	Detonation Tem-perature, °C
19.3	164
20.4	160
27.5	159

Table III

STABILITY OF NH ClO_4-N_2H_4 MIXTURES AT ABOUT 100°C

% NH_4ClO_4	Time Interval, min	Detonation Tem-perature, °C
21.3	95.5	109
18.0	40	101
18.9	57.5	98
20.7	42.5	102
23.5	22	98
22.8	18 hr at 80°C	did not detonate

FREEZING POINT DETERMINATIONS

The freezing point is defined as being identical with the melting point; the melting point is taken as the temperature when the last particle of frozen material vanishes, or when the temperature of the medium detectably increases at constant energy input. Other, more precise definitions could be given, but the ones noted here apply to the experimental procedure adopted in this work. For example, if one measures the "freezing point" of a liquid by cooling it slowly until it is supercooled and the viscosity increases so much that it is essentially immobile ("pour point"), then the ammonium perchlorate-hydrazine solutions used in this work can be said to have much lower "freezing points" than indicated by disappearance of the last particle of frozen material. Although "pour-point" favors a mixture when it is considered as a candidate monopropellant, the fact that crystallization or freezing out of a solid phase is always possible through nucleation or agitation in the rocket-engine pumps or propellant distribution system makes it necessary to use disappearance of the last particle as a criterion for propellant freezing point determinations. Freezing points measured in this way provide assurance that blockage of injector ports and the like will not occur.

The usual methods for determining the freezing points of various compounds require proximity of the operator to the apparatus employed and the solutions that are being measured. In order to determine the freezing points of the potentially-explosive mixtures of ammonium perchlorate and hydrazine, equipment was fabricated that could be operated remotely without sacrificing accuracy of data. The insidious nature of hydrazine perchlorate was recognized from the start of this work, and precautions were taken to protect the operator from the explosion hazard presented by the triboelectrical ignition of crystals which inevitably separate at the freezing point.
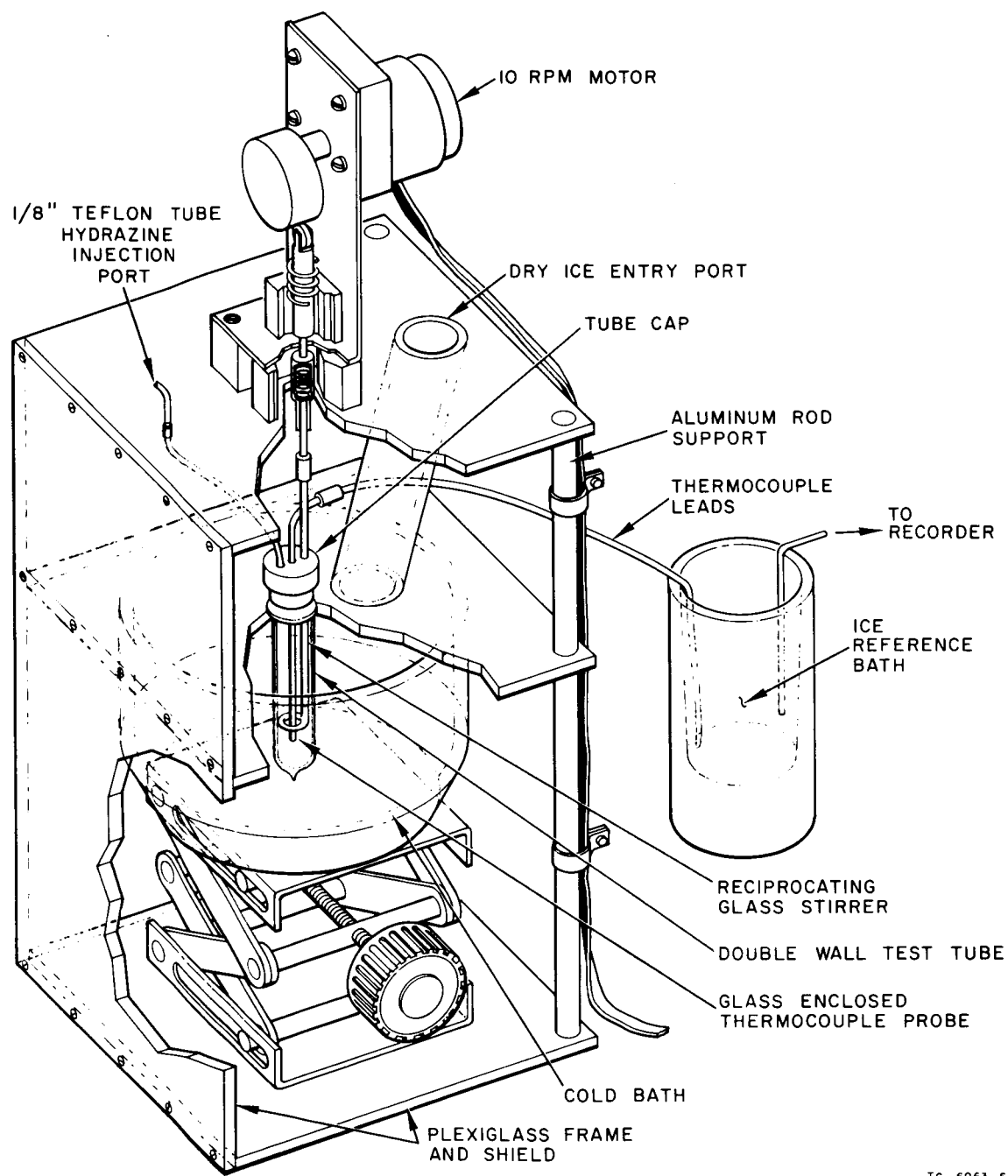
The freezing points of solutions ranging from a concentration of 0% to 30% ammonium perchlorate in hydrazine were measured by means of

14

a 5-thermel system which was calibrated against pure materials of accepted freezing-point values.

The over-all design of the freezing-point apparatus is shown in Figure 5. A 10-rpm motor with a cam and spring-loaded follower was used to obtain the up-down stirring action found to be most suitable for these determinations. The spring-loaded follower permitted the stirrer to be frozen rigidly without damaging the motor or other parts of the apparatus. The reciprocating glass stirrer surrounded the glass-enclosed thermocouple probe, which contained five 2-mil thermocouples wired in series to increase the thermoelectric output to values which could easily be measured by a 1-mv recorder. The space within the double-walls of the sample tube was evacuated; this permitted the sample to be cooled and warmed at a slow rate. The sample tube was initially charged with ammonium perchlorate, and the Teflon injection port was used for the introduction of hydrazine; in this way, accurate mixtures were prepared without hazard. A Lab-Jack was used to raise and lower the cold bath; Dry Ice was added through the entry port at the rear of the apparatus as required.

Continuous temperature measurement was made possible by thermopiles consisting of five copper-constantan couples in series; a reference thermopile was kept at ice temperature. Since the signal generated was often greater than 1 millivolt, a precision potentiometer was used as a variable source to "buck" the output and leave an effect of less than 1 mv. The recorder and potentiometer were located at some distance away from the freezing-point apparatus.

By noting the bucking voltage from the potentiometer and the voltage indicated by the recorder, a precise determination of the signal being generated by the thermopile could be determined at any time. Since the reference side of the thermopile was maintained at $0^{o}C$, and the temperature was measured over a wide range above and below $0^{o}C$, a reversing switch was placed in the circuit to make possible recording of the freezing point curve on a "left-zero" recorder.

10 RPM MOTOR

1/8" TEFLON TUBE
HYDRAZINE
INJECTION
PORT

DRY ICE ENTRY PORT

TUBE CAP

ALUMINUM ROD
SUPPORT

THERMOCOUPLE
LEADS

TO
RECORDER

ICE
REFERENCE
BATH

RECIPROCATING
GLASS STIRRER

DOUBLE WALL TEST TUBE

GLASS ENCLOSED
THERMOCOUPLE PROBE

COLD BATH

PLEXIGLASS FRAME
AND SHIELD

TC-6063-6

FIG. 5   FREEZING POINT APPARATUS

Because the determinations of the freezing points of hydrazine-ammonium perchlorate mixtures were considered hazardous (sensitivity of solid hydrazine perchlorate), the operator was protected by heavy Plexiglas (Figure 5) and the apparatus was located in a hood. The hood door was kept closed as much as possible during the determinations.

A sample of ammonium perchlorate was weighed into a previously-dried double-walled test tube and placed in position in the apparatus, and the stirring motor was turned on. A dry, 10-ml gas-tight syringe was partially filled with about 3 ml of hydrazine and weighed. The hydrazine was injected into the sample tube via the Teflon entry port, and the syringe re-weighed.

The ammonium perchlorate was allowed to dissolve, and the freezing point of the solution was determined (see Figure 6). At completion of the determination, water was injected into the sample tube to dilute the solution and render it insensitive to shock. After the water was added, the apparatus was disassembled and cleaned.

In general, all of the hydrazine-ammonium perchlorate mixtures became quite viscous and eventually froze into glassy masses. Super-cooling was always evident, but the efficiency of stirring was such that it was kept at a minimum. Without stirring, the mixtures supercooled into viscous liquids, and temperatures as much as 20 to 30 degrees below the freezing point could be observed.

The data obtained from the determination of the freezing points of a series of solutions of ammonium perchlorate in hydrazine are plotted in Figure 7; the actual numerical values are recorded in Table IV. The expected freezing points (based on ideal solution behavior) were computed as follows:

FIG. 6   TYPICAL FREEZING POINT CURVE

18
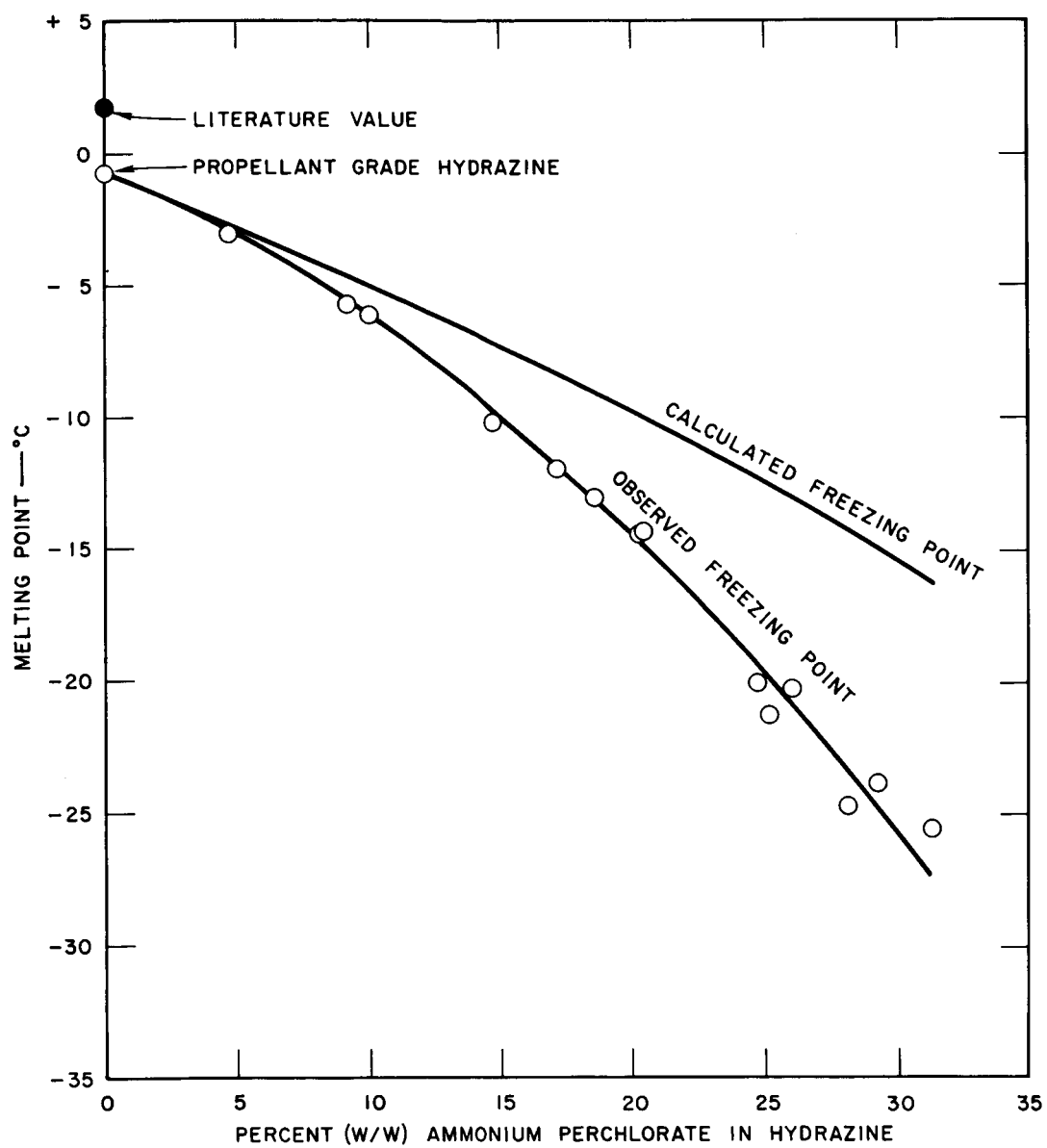
FIG. 7 OBSERVED AND CALCULATED MELTING POINTS OF SOLUTIONS OF NH_4ClO_4 IN NH_2H_4

Table IV

OBSERVED AND CALCULATED MELTING POINTS
FOR AMMONIUM PERCHLORATE-HYDRAZINE SOLUTIONS

% NH_4ClO_4	% N_2H_4	N_s	Observed Melting Point, °C	Calculated Melting Point °C
0.00	100.00	1.00000	(+ 1.65)*	--
0.00	97.87	0.94963	- 0.90	- 0.89
4.44	93.52	0.91469	- 2.78	- 2.70
4.61	93.36	0.91333	- 3.09	- 2.77
5.68	92.31	0.90478	- 3.05	- 3.23
9.06	89.00	0.87714	- 5.75	- 4.68
9.99	88.09	0.86017	- 6.11	- 5.11
14.71	83.47	0.82848	-10.21	- 7.28
17.18	81.06	0.80623	-12.00	- 8.51
18.49	79.77	0.79439	-13.05	- 9.16
20.20	78.10	0.77895	-14.48	-10.01
20.34	77.96	0.77780	-14.41	-10.09
24.61	73.78	0.73656	-20.10	-12.32
25.15	73.26	0.73132	-21.34	-12.58
25.87	72.55	0.72413	-20.27	-13.09
28.00	70.47	0.70286	-24.80	-14.16
29.07	69.42	0.69191	-23.95	-14.92
31.19	67.34	0.66967	-25.61	-16.27

* Literature value.

From the Clausius-Clapeyron equation it can easily be shown that

$$\Delta T = T_f - T_s = \frac{RT_f T_s}{\Delta H_s^f} \ln N_s$$

where

ΔH_s^f = 3.025 kcal/mole, the heat of fusion of the solute, hydrazine

T_f = the freezing point of the solution

T_s = the freezing point of the solute, 274.8°K.

Hence,

$$\Delta T = \frac{1.987(274.8)2.303}{3025} T_f \log N_s$$

$$= 0.41570 \ T_f \log N_s$$

From the melting point of the hydrazine used as the solute, $-0.90^{\circ}C$, and the assigned melting point of $+1.65^{\circ}C$ for pure hydrazine, it was ascertained that the mole fraction of hydrazine must be 0.9496, and since the composition of the hydrazine by actual analysis was known, the following must be the effective molality of the impurities within it:

$$\left.\begin{array}{ll} H_2O & 1.91\% \\ NH_3 & 0.06 \\ Aniline & 0.16 \end{array}\right\} \quad 0.162 \text{ mole (effective)}$$

$$\text{Hydrazine} \quad 97.87 \quad \underline{3.054 \text{ moles}} \approx 0.9496 \text{ mole fraction}$$

$$\Sigma_m = 3.216$$

Hence, in the preparation of solutions of ammonium perchlorate (assumed H_2O content = 0) in hydrazine, the 0.162 effective moles of impurities would be included in the final mixtures in the proportion expected from the weights of hydrazine used. Further, since the reaction of ammonium perchlorate with hydrazine is assumed to go to completion to form hydrazinium perchlorate and ammonia, the total moles in solution is expressed as

$$\Sigma_m = M_{N_2H_4} + 2M_{NH_4ClO_4} + M_{impurities}$$

and the moles of hydrazine in solution:

$$M_{N_2H_4} - M_{NH_4ClO_4} = M_s$$

The mole fractions of hydrazine, thus, are given by:

$$\frac{M_s}{\Sigma_m} = N_s \qquad .$$

The melting point depressions, ΔT, can be simply computed; they are given in Table IV for the compositions used in the experimental determination of the freezing points, and are plotted in Figure 7 for comparison. The great deviation between observed points and computed points is not at all unexpected, for the derivation of the equations used in computing freezing points is based on the assumptions of ideal solutions, constancy of heat of fusion, and that the effective molality of the impurities in hydrazine remain constant. Perhaps the greatest error that can be anticipated is that the calculated values are based on the separation of solid hydrazine from the solutions as they freeze (or hydrazine crystals are the last to melt); analysis of the separated phase is needed to resolve this point. The agreement of calculated and observed data at low concentrations of ammonium perchlorate (less than about 5% W/W) is expected, and the large deviations at the 30% level are customarily found when the mole fraction of the solute nears 0.50 in nonideal solutions. A plot of the melting points as a function of the mole fraction of hydrazine is essentially similar to Figure 7.

CONCLUSIONS

The long-term storage tests of ammonium perchlorate-hydrazine solutions at elevated temperatures indicate that the solutions are stable for seven months at 75°C for a 10% solution, 60°C for a 20% solution, and at 52°C for a 30% solution.

The thermal-stability bomb tests indicate that a 20% ammonium perchlorate-hydrazine mixture can be maintained at 80°C for at least 18 hours, but that detonations occur within a few minutes of heating at about 100°C.

The proximity of the 80°C temperature for short-term storage of a 20% NH_4ClO_4-N_2H_4 mixture to the 60°C temperature for a long-term

storage implies that as a safety factor, propulsion equipment should be designed to maintain temperatures not to exceed those indicated by the long-term storage tests:

% NH_4ClO_4 in N_2H_4	Maximum Storage Temperature, ^oC
10	75
20	60
30	52

The freezing points of solutions of ammonium perchlorate in hydrazine are anomalous; a 30% solution becomes viscous and begins to freeze at about -25^oC into a glassy solid.